Transient Infrared Photoreflectance Study of Superconducting MgB_2: Evidence for Multiple Gaps and Interband Scattering

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(Dated: February 2, 2008)

We studied the far-infrared reflectance of superconducting MgB_2 in and out of equilibrium using pulsed synchrotron radiation. The equilibrium data can be described by a single energy gap at $2\Delta/hc = 43$ cm^{-1}. The fit improves slightly at lower frequencies when two gaps (at 30 cm^{-1} and 56 cm^{-1}) are assumed to exist. The non equilibrium data is obtained when excess quasiparticles are generated in the MgB_2 film by a laser pulse, decreasing the energy gap(s). The temperature dependence of the number of excess quasiparticles indicates that only a single gap near 30 cm^{-1} controls the non-equilibrium process. Fits to the photo-induced reflectance show the presence of the two gaps but weakening of an energy gap at 30 cm^{-1} only. Our data can be understood if one considers the picture where excited quasiparticles created by the laser impulse relax to the lowest gap band before recombining into Cooper pairs.

PACS numbers: 74.40.+k, 74.25.Gz, 78.47.+p, 74.70.Ad

The heat capacity of MgB_2 was known down to 20 K since 1957 but the sparse data set did not make the superconducting transition clear [1]. More recently, detailed data revealed superconductivity in this compound with a remarkably high critical temperature [2] for a system showing a classical electron-phonon coupling mechanism. The calculated Fermi surface for MgB_2 has two separate pieces — a 2D (σ) and a 3D (π) bands [3]. Liu *et al.* [4] propose that two energy gaps (Δ_π and Δ_σ) exist for these two portions of the Fermi surface and predicted that $\Delta_\sigma \approx 3\Delta_\pi$. This picture is supported by experiments such as tunneling [5], Raman spectroscopy [6], heat capacity [7] and angle-resolved photo-emission [8]. Tunneling data also shows that in the superconducting state the two bands undergo the superconducting transition at the same temperature [5].

Two-band superconductivity is an interesting problem that has been addressed by Suhl *et al.* [9]. They showed that for non-interacting bands two critical temperatures exist. If a very small interaction between the bands is turned on, the whole system shows a superconducting transition at the highest $T_c$while preserving the two gaps. Recent calculations [10] showed that this weakly interaction scenario applies to MgB_2. However the mechanism and size of the interaction remain speculative. Infrared spectroscopy on MgB_2 [11, 12, 13, 14, 15] did not provide any clear cut picture about the presence of two bands in MgB_2 although the data does not seem to follow strictly the BCS theory.

In this letter we report an infrared reflectance study of a MgB_2 thin film, including the transient change in reflectance that results when a laser pulse produces excess quasiparticles in the film. We find that the conventional reflectance spectrum can be roughly described by an optical conductivity based on a single energy gap near 43 cm^{-1}. However, the agreement between theory and experiment improves at low frequencies if one assumes two energy gaps at 30 and 56 cm^{-1}. The transient photo-reflectance technique senses how the energy gap changes due to an excess population of quasiparticles. The temperature dependence of this excess quasiparticle signal obtained from the time dependent changes in the photo-reflectance measurements on the same film is fully described by a single energy gap at 30 cm^{-1}, in apparent contradiction with the conventional reflectance results. This discrepancy is resolved by the photo-reflectance spectrum that indicates the presence of at least two energy gaps in the system with the non-equilibrium dynamics dominated by the smaller energy gap.

The sample for our study was a thin film of MgB_2 on a sapphire substrate [16]. The film is estimated to be about 30 nm thick and highly oriented with the c-axis normal to the substrate surface. Typical of many thin superconducting films, the T_c of 30 K is suppressed compared to bulk material ($T_c = 39$ K) [11, 12]. Upon cooling, the electrical resistance decreases slightly, indicating metallic behavior dominated by impurity-type carrier scattering. Standard reflectance measurements were performed using the Bruker IFS 66v FTIR spectrometer at beamline U10A of the NSLS, with synchrotron radiation as the IR source. The specimen was solidly clamped with indium gaskets to the copper cold-finger of a heli-tran cryostat, leaving a 3 mm diameter aperture exposed for the IR measurement. The remaining 80% of the sample's surface was available for thermal conduction into the cold finger. The far-infrared reflectance from the film was measured

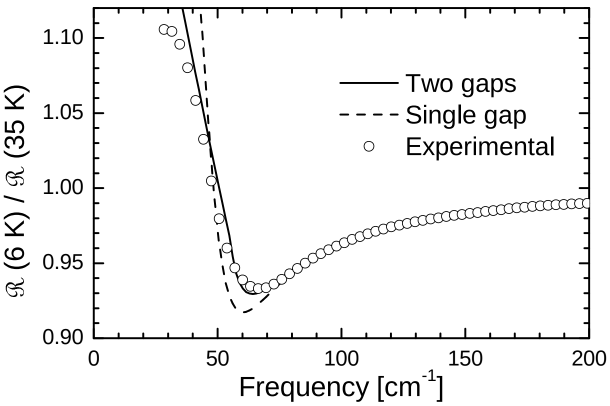

FIG. 1: Measured ratio of $\mathfrak{R}(T = 6\ \mathrm{K})/\mathfrak{R}(T = 35\ \mathrm{K})$ for a MgB_2 film (open circles). The lines are fits assuming either a single gap $2\Delta = 43\ \mathrm{cm}^{-1}$ (dashed curve) or a simple two gap model (solid curve) with $2\Delta_\pi = 30\ \mathrm{cm}^{-1}$ (55 %) and $2\Delta_\sigma = 56\ \mathrm{cm}^{-1}$ (45%). In both fits we used $R_\square = 18\ \Omega$; $\tau^{-1} = 300\ \mathrm{cm}^{-1}$ and 3.05 as the refraction index for the sapphire substrate.

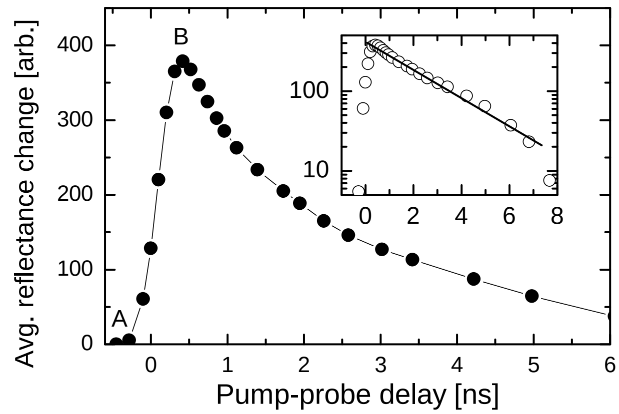

FIG. 2: Spectrally averaged change in the film reflectance as a function of time due to a short laser pulse. The average laser power used was 20 mW corresponding to 0.4 nJ per pulse. Two points (A and B) mark the moment just prior to the pulse (no excess quasiparticles) and at the peak signal (end of laser pulse, maximum excess quasiparticle density). The inset shows the same data in a semi-log plot. Within experimental error only a single exponential decay can be seen in the data.

at a variety of temperatures below T_c (superconducting state) and at $T = 35$ K (normal state).

The ratio of the normal state to the superconducting reflectivity at 6 K, $\mathfrak{R}_S/\mathfrak{R}_N$, is shown in Fig. 1 as open circles. The lines are fits to the reflectivity using an expression for the reflectance of a thin film on a transparent substrate in terms of the film's optical conductivity

$$\mathfrak{R} = \frac{(n - 1 + y_1)^2 + y_2^2}{(n + 1 + y_1)^2 + y_2^2} \tag{1}$$

where n is the substrate's refractive index and $y = (4\,\pi/c)\hat{\sigma}d$ is the film's dimensionless complex admittance with $\hat{\sigma}$ the optical conductivity and d the film thickness [17]. This expression is valid when d is smaller than the penetration depth. Measurements of the film sheet resistance indicate a penetration depth of about 100 nm at $50\ \mathrm{cm}^{-1}$, which is smaller than the thickness by about a factor of 3. If we assume the reflectance is characteristic of a bulk metal, i.e. thick film, plausible fits to the data can not be achieved. Still, the film's transmission is less than 1%, so contributions from multiple internal reflections in the substrate are negligible and not included in this expression. The solid line is a calculation for $\mathfrak{R}_S/\mathfrak{R}_N$ using the expressions of Zimmermann *et al.* [18] for the optical conductivity of a BCS superconductor including the effects of finite scattering. It assumes a single gap $2\Delta = 43\ \mathrm{cm}^{-1}$. The solid line in Fig. 1 assumes a simple model for two gaps, $2\Delta_\pi = 30\ \mathrm{cm}^{-1}$ and $2\Delta_\sigma = 56\ \mathrm{cm}^{-1}$. Here, the optical conductivity is calculated using $\hat{\sigma} = f\hat{\sigma}_\pi + (1 - f)\hat{\sigma}_\sigma$ where $\hat{\sigma}_\pi$ and $\hat{\sigma}_\sigma$ are the optical (complex) conductivity for a superconductor having energy gaps $2\Delta_\pi$ and $2\Delta_\sigma$, and f is the spectral weight of the π (3D) band. This picture is valid for two non-interacting sets of carriers responding in parallel. Drude fits to the normal state yielded a scattering rate of about $300\ \mathrm{cm}^{-1}$. Although the 2 gap model better describes the data at low frequencies, the improvement is not sufficient to conclude that two gaps must exist.

Transient far-infrared photo-reflectance measurements were also performed using the same spectrometer and beamline. Here, we measured the reflectance change due to illuminating the MgB_2 film with 2 ps near-infrared ($\lambda = 760$ nm) pulses from a Ti:sapphire laser. The laser pulses break pairs and weaken the superconducting state for a brief amount of time (≈ 1 ns) [19]. The resulting change in reflectance is sensed with the ≈ 1 ns infrared pulses from the synchrotron in a pump-probe configuration. The average laser power was 20 to 50 mW (0.4 to 1 nJ per pulse) in a spot filling the whole 3 mm sample aperture. The pulse repetition frequency was 53 MHz, matching the pulsed IR output from the synchrotron. For time-dependent studies, the broadband probe pulses were not spectrally resolved, and the response is an average of the reflectance across the 10 to $100\ \mathrm{cm}^{-1}$ spectral range. An analysis of the time dependent transient photo-reflectance gives us a good estimate of the effective pair recombination rate [20]. Figure 2 shows the average reflectance change as a function of the delay between pump and probe pulses at 6 K. In accordance with other BCS superconductors [19, 20] the effective recombination time is found to be a few nanoseconds. For comparison, high-T_c materials have a much faster dynamics, lying in the picosecond range [21]. One important remark is that, within the experimental time resolution, no evidence of multiple decays is found. In fact, ultra-fast pump-probe measurements on MgB2 [22, 23, 24] do not find any ev-

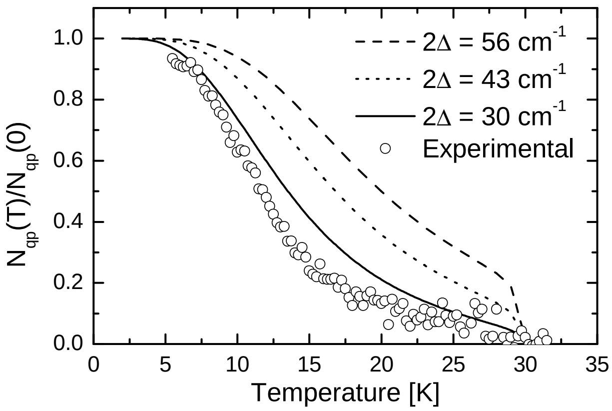

FIG. 3: Temperature dependence of the peak photo-induced reflectance signal of Fig. 2 (point B). The signal is approximately proportional to the number of excess quasiparticles. Also shown are calculations of the excess quasiparticle fraction determined using the following parameters (adopting [25] notation): $N(0) = 24x10^{21}$ eV^{-1}; $N = 11x10^{22}$ cm^{-3}; $10^3 b = 0.044$ meV^{-2}; and $<\alpha^2>= 0.56$ meV. For $2\Delta_\pi =$ 30 cm^{-1} we used $Z_1(0) = 1.45$; for $2\Delta_\sigma = 56$ cm^{-1} we used $Z_1(0) = 2.1$ and for $2\Delta = 43$ cm^{-1} we used the average value $Z_1(0) = 1.78$. We chose to keep the same gaps used in the equilibrium calculation but the data description can be improved if one uses 25 cm^{-1} instead of 30 cm^{-1}.

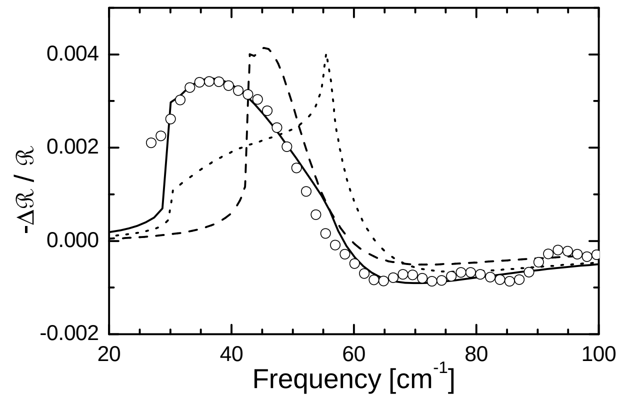

FIG. 4: Photo-induced change in reflectance due to pair breaking by a 1 nJ laser pulse (circles). This spectrum is measured between points A and B in Fig. 2. The lines are simulations assuming that the photo-induced state can be calculated by the difference between two BCS reflectivity spectra with slightly different gaps. All the parameters used in the fit of Fig. 1 are kept here. The dashed line assumes the single average gap picture and uses a gap shift of 0.18 cm^{-1} in the photoexcited state. The dotted line is the simulation for a two gap system where both gaps shrink in the photoexcited state. We used -0.2 cm^{-1} and -0.38 cm^{-1} for the shifts in $2\Delta_\pi$ and $2\Delta_\sigma$, respectively (corresponding to a 0.7 % gap shift in each electron system). The solid curve also uses two gaps but assumes that only the π gap shifts (by -0.65 cm^{-1}) in the photoexcited state.

idence for more than one relaxation time related to superconductivity down to the ps regime.

The amplitude of the time resolved signal is proportional to the number of excess quasiparticles in the system N_{qp}. Its thermal dependence is shown in Fig. 3. Assuming a single gap in the system, we can calculate $N_{qp}(T)$ from energy conservation considerations obtaining $N_{qp}(T)/N_{qp}(0) = [\Delta(0)/\Delta(T)]/(1+2\tau_B/\tau_R)$ [20]. We utilized the expressions from Kaplan *et al.* [25] to calculate the pair recombination time τ_R and the pair breaking time by phonons τ_B. The parameters we used in Kaplan's formalism were determined from ref. [4]. This single gap picture describes very accurately the data as far as we use the small gap value obtained in the two component fit for the reflectivity. For comparison, we also show in this figure the calculations using the average and the highest σ gaps.

The gap value used in the thermal dependence of N_{qp} is in direct contradiction with the equilibrium reflectivity parameters. In the latter, regardless of the model used, a gap value around 50 cm^{-1} is present whereas only a single gap at 30 cm^{-1} describes $N_{qp}(T)$. To address this problem we looked into the photo-reflectance spectra, shown in Fig. 4. Measurements were made with the laser pulses and synchrotron pulses in coincidence and again with the pulses 17 ns away from coincidence. From these we calculated the transient photo-reflectance as $-\delta\mathcal{R}/\mathcal{R} = -(\mathcal{R}_{0\text{ns}} - \mathcal{R}_{17\text{ns}})/\mathcal{R}_{17\text{ns}}$, which essentially eliminates any overall thermal effects from laser heating. The degree of laser heating could be estimated by measuring the reflectance change between laser on and off, and compared with measurements of the actual temperature-dependent reflectance. The average temperature rise was less than 1 K. A detailed description of non-equilibrium spectroscopy using our pulsed laser and synchrotron set up can be found in Ref. [26].

The direct consequence of pairs broken by a laser pulse with the creation of excess quasiparticles is a weakening of the superconducting state [27]. This weakened state can be spectroscopically detected and resolved as a slightly reduced energy gap [20] allowing the transient photo-reflectance data to be analyzed using the same expressions as those of the equilibrium reflectance. The dashed curve in Fig. 4 assumes that the system has a single gap at 43 cm^{-1} which is decreased by photoexcitation. Although the amplitude and overall shape of the signal can be reproduced by this simulation, quantitative agreement is not achieved. The dotted line assumes that the system has the same two gaps used in the equilibrium reflectance fit and that in the photo-excited state both gaps shrink by an amount consistent with a small raise in the electronic temperature. The introduction of this second gap does not improve the data description and, actually, introduces new features absent from the data. Our third approach, depicted by the solid line, assumes that the system does have two gaps but

that only the smaller energy gap shrinks in the photo-excited state. This is the behavior one would expect if, after pair-breaking by the laser, the excess quasiparticles are left primarily in the system having the smaller energy gap, i.e., quasiparticles are "transferred" from the σ band (larger gap) to the π band (smaller gap) before the recombination is completed. Such a picture reconciles completely the whole set of data, equilibrium and non equilibrium.

We can imagine two qualitatively different processes that allow for the recombination to occur within the lowest gap band only: (i) a transfer of the actual quasiparticles (scattering) or (ii) a transfer of energy from the σ to the π band. In the following we discuss such processes.

When talking about transfer of quasiparticles one could argue for impurity scattering diffusing quasiparticles between the bands. The π band, having a smaller gap is energetically favorable and quasiparticles settling to its gap edge would be incapable of returning to the σ band. This process, however, implies a very large connection between the bands. In this case, MgB_2 should show only an average gap in the equilibrium measurements in disagreement with STM data, for instance [5].

An alternative is to think in terms of energy transfer instead of quasiparticle transfer between the bands. Photo-exciting such a system with a near-IR laser pulse will create quasiparticle excitations in both bands. As before, these high energy excitations relax by creating lower energy quasiparticles and phonons. Looking at the Fermi surfaces, we note that whereas the π band spans most of the Brillouin zone, the σ bands are confined to cylinders around the $\Gamma - A$ direction. Therefore, only umklapp processes and phonons with momentum along the $\Gamma - A$ direction will be able to break other pairs in the σ band. We can safely assume that phonons created in the relaxation to the gap edge will most likely generate unpaired quasiparticles in the π band. In addition, quasiparticles that relax to the σ band gap edge will recombine and create $2\Delta_\sigma$ phonons that, once again can readily break pairs in the π band. The resulting quasiparticles can scatter and settle to an energy Δ_π and recombine. In addition to the restricted Brillouin zone access to the σ band, phonons produced by recombination in the π band lack energy to break pairs in the σ band. All in all, both intraband relaxation and quasiparticle recombination in the σ band contribute to increase the π population but the opposite process does not happen. Therefore the phonon bottle-neck to recombination only occurs for the smallest gap in the system, and the excess quasiparticles quickly settle to this gap edge while the quasiparticle density in the larger gap band returns to its equilibrium value. The very presence of two different energy gaps implies that an excess quasiparticle density in one system will preferentially weaken that system over the other. Thus we expect that only the smallest energy gap in the system will experience the gap reduction described by Owen and Scalapino [27].

The absence of a two component decay in the time dependent photo-induced signal can be explained by the small amount of quasiparticles that recombine in the σ band. A cascading effect makes that each quasiparticle excited by the laser photons (energy $h\nu$) creates $h\nu/2\Delta$ quasiparticles at the gap edge. The "energy transfer" process proposes that the quasiparticles created by the cascading appear at the π band. This gives us 500 times more quasiparticles in the π than in the σ band at the beginning of the recombination and make it very unlikely to see a fast relaxation due to the σ band pair recombination.

Recent inelastic x-ray scattering data [29] shows that the E_{2g} phonon is anomalously broadened along the $\Gamma - A$ direction in the Brillouin zone, the same direction of the σ bands. The origin of this broadening is related to a strong coupling between this phonon and σ electrons [30]. Recent calculations show the importance of band coupling through phonons [31, 32] and we propose the E_2g phonon to be the natural candidate for the mediator of the energy transfer processes described above.

In this letter we showed static and photo-induced far infrared measurements on a MgB_2 film. Whereas the equilibrium spectrum indicate a superconducting gap around 50 cm^{-1}, the non equilibrium dynamics is dominated by a gap at 30 cm^{-1}. The two sets of data are compatible if one considers the picture where excited quasiparticles created by the laser impulse relax to the lowest gap band before recombining into Cooper pairs. This can be achieved by phonon scattering considering that the π band covers a much larger volume of the Brillouin zone than the σ band. We propose to assign the E_{2g} phonon as the mediator of this process.

This work was performed with the support of the U.S. Department of Energy through contract DE-ACO2-98CH10886 at the NSLS. Operation of the synchronized laser system is also supported by DOE through contract DE-FG02-02ER45984 with the University of Florida. We are grateful to P.B. Allen, J. Carbotte, T. Devereaux, M.V. Klein, I.I. Mazin, A.J. Millis, P. Monod, M.R. Norman, E. Nicol and D.B. Tanner, for useful discussions.

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